<Division of Environmental Chemistry>Chemistry for Functionalized Surfaces

Division of Environmental Chemistry
– Chemistry for Functionalized Surfaces –

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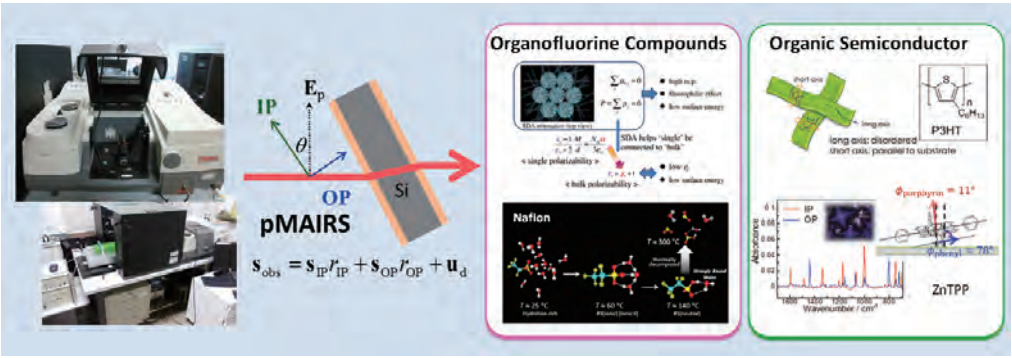
Scope of Research

To understand the chemical structure and properties of a molecular aggregated system, the keywords of molecular interactions and orientation are focused on, and the molecular aggregates are investigated by using originally developed spectroscopic techniques. The current major topics are: (1) perfluoroalkyl-specific properties in a condensed system; (2) controlling factors of molecular packing and orientation in a thin film of an organic semiconductor compound; (3) development of new molecular orientation analytical technique "MAIRS2."

KEYWORDS

Infrared and Raman Spectroscopy
Surface and Interface Chemistry
Perfluoroalkyl Compounds
Organic Semiconductors
pMAIRS and MAIRS2



Selected Publications

Shioya, N.; Murdey, R.; Nakao, K.; Yoshida, H.; Koganezawa, T.; Eda, K.; Shimoaka, T.; Hasegawa, T., Alternative Face-on Thin Film Structure of Pentacene, *Sci. Rep.*, **9,** 579 (2019).

Nakamura, T.; Shioya, N.; Shimoaka, T.; Nishikubo, R.; Hasegawa, T.; Saeki, A.; Murata, Y.; Murdey, R.; Wakamiya, A., Molecular Orientation Change in Naphthalene Diimide Thin Films Induced by Removal of Thermally Cleavable Substituents, *Chem. Mater.*, **31,** 1729-1737 (2019).

Shimoaka, T.; Sonoyama, M.; Amii, H.; Takagi, T.; Kanamori, T.; Hasegawa, T., Raman Optical Activity on Solid Sample: Identification of Atropisomers of Perfluoroalkyl Chains Having a Helical Conformation and No Chiral Center, *J. Phys. Chem. A*, **123,** 3985-3991 (2019).

Shioya, N.; Tomita, K.; Shimoaka, T.; Hasegawa, T., Second Generation of Multiple-Angle Incidence Resolution Spectrometry, *J. Phys. Chem. A*, **123,** 7177-7183 (2019).

Wang, C.; Sharma, S. K.; Olaluwoye, O. S.; Alrashdi, S. A.; Hasegawa, T.; Leblanc, R. M., Conformation Change of α-Synuclein(61−95) at the Air-Water Interface and Quantitative Measurement of the Tilt Angle of the Axis of its α-Helix by Multiple Angle Incidence Resolution Spectroscopy, *Colloids Surf. B*, **183,** 110401 (2019).

Sakakibara, K.; Nishiumi, K.; Shimoaka, T.; Hasegawa, T.; Tsujii, Y., pMAIRS Analysis on Chain-End Functionalization of Densely Grafted, Concentrated Polymer Brushes, *Macromolecules*, **52,** 6673-6682 (2019).

Alternative Face-on Thin Film Structure of Pentacene

Rod-shaped molecules represented by pentacene are known to form a highly ordered structure in a thin film, in which the molecular long axis aligns perpendicularly to the substrate surface, *i.e.*, end-on orientation. The face-on oriented thin film, on the other hand, where the molecular plane is parallel to the substrate, has never been found on an inert substrate represented by SiO_2. As a result, the face-on orientation has long been believed to be generated only on specific substrates such as a metal single crystal. In the present study, the face-on orientation grown on a SiO_2 surface has first been identified by means of visible and infrared p-polarized multiple-angle incidence resolution spectrometry (pMAIRS). The combination of the multiple techniques reveals that the face-on phase is definitely realized as the dominant component. The face-on film is obtained when the film growth is kinetically restricted to be prevented from transforming into the thermodynamically stable structure, *i.e.*, the end-on orientation. This concept is useful for controlling the molecular orientation in general organic semiconductor thin films.

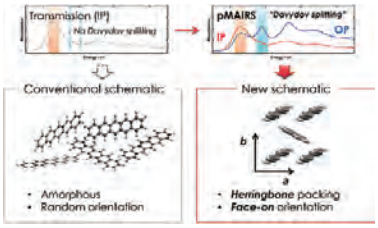


Figure 1. Face-on thin-film structure of pentacene revealed by Vis pMAIRS.

Raman Optical Activity on a Solid Sample: Identification of Atropisomers of Perfluoroalkyl Chains Having a Helical Conformation and No Chiral Center

Perfluoroalkyl (R_f) chains have a specific helical conformation due to the steric repulsion between the adjacent CF_2 units. Although R_f chains have no chiral center, two chiral structures, *i.e.*, the right-handed (R) and left- handed (L) helices, are available as the most stable conformations, which are atropisomers to each other. According to the stratified dipole array (SDA) theory, the helical structure about the chain axis plays a key role in the spontaneous molecular aggregation of R_f chains in a two-dimensional manner, and the R_f chains having the same chirality tend to be aggregated spontaneously to generate molecular domains. This implies that an R_f compound in a solid state should be a mixture of the R and L domains, and each domain should exhibit distinguishable optical activity. To identify molecular domains with different atropisomers, in this study, Raman optical activity (ROA) measurements were performed on a Raman imaging spectrometer. Through the ROA measurements of recrystallized solid samples of an R_f compound, each particle exhibits an apparent optical activity, and the two atropisomers were readily distinguished. As a result, an R_f compound with the same helicity is found to be spontaneously aggregated as expected by the SDA theory.

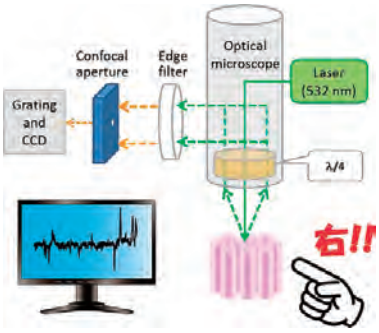


Figure 2. Overall view of the apparatus for Raman and ROA measurements.

Second Generation of Multiple-Angle Incidence Resolution Spectrometry

Infrared (IR) surface spectroscopic techniques commonly have long-term issues that 1) the multiple reflections of light in the substrate yield optical interference fringes in the absorption spectrum, and 2) the double-modulation of light at the interferometer in FT-IR makes a water-vapor-subtraction impossible. These measurement troubles often disturb the quantitative analysis of chemical bands of the analyte thin film. To overcome the long-term common issues, in the present study, an advanced MAIRS technique named "MAIRS2" is proposed: the angle of incidence is fixed at a larger angle to avoid the two problems; whereas the polarization angle is changed instead. With this simple conceptual change of MAIRS, as a result, we are ready for concentrating on spectral analysis only without concerning about the measurement troubles.

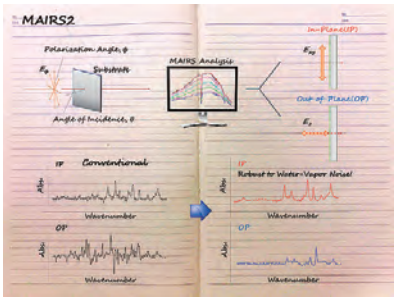


Figure 3. MAIRS2 realizes ideal IR measurements of a thin film for accurate molecular orientation analysis, which is highly robust to water-vapor and optical fringes.